

Non-Conventional Fe₃C-based Nanostructures

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Supporting information

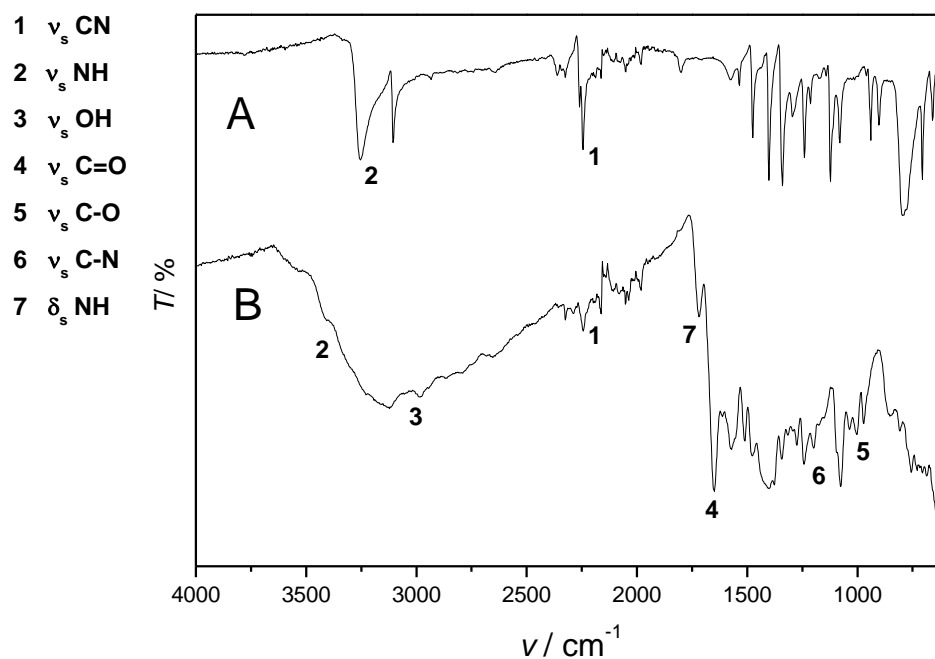


Figure 1. IR-spectra of A) solid DI and B) iron-DI sample at R=1

Tab. 1: d_{spacing} values obtained by Fourier transform of the HR-TEM pictures. The calculated values and relative hkl index for Fe_3C^* are also reported.

compound	$d_{\text{meas}}[\text{Å}]$	$d_{\text{calc}}^*[\text{Å}]$	hkl
Fe_3C	2.0	2.01	031
	2.2	2.26	002
	3.0	3.02	111
	2.7	2.54	200

*Ref. ICDD-PDF4+ 00-035-0772 (Fe_3C)

Tab. 2: Mössbauer hyperfine parameters for FeDI1 samples prepared at 700°C

	Doublet site			Sextet site			
	δ (mm/s)	Δ (mm/s)	RA (%)	δ (mm/s)	Δ (mm/s)	H (T)	RA (%)
FeDI1	0.86	2.25	57	0.06	0.01	20.8	43

δ -Isomer shift relative to α -iron, Δ -Quadrupole splitting, RA-Relative Absorption area, H-Hyperfine field. Uncertainties are ± 0.02 mm/s for δ and Δ , ± 0.3 T for H and 2% (absolute) for RA.

In order to obtain a better understanding of the carbon phase accompanying the iron carbide, a sample was treated with concentrated HCl to separate the pure carbon from the carbide. In particular, 1 ml of HCl20% was added to a weighted amount of Fe_3C black magnetic powder (108.6 mg). The mixture was left to react for one week followed by removal of a deep yellow and clear supernatant phase. The residual powder (black and not magnetic) was washed twice with ethanol, dried and reweighed (38.0 mg). The mass loss was ~60 – 65 %.

The XRD pattern of the resulting sample is shown in figure 2. Only a graphitic pattern (main peaks at 26 and 45 degrees) is observed. For comparison the spectrum of the sample before the acid treatment is also reported. The main carbon peak is shifted to a lower angle suggesting that residual carbon is somehow bonded to the Fe_3C .

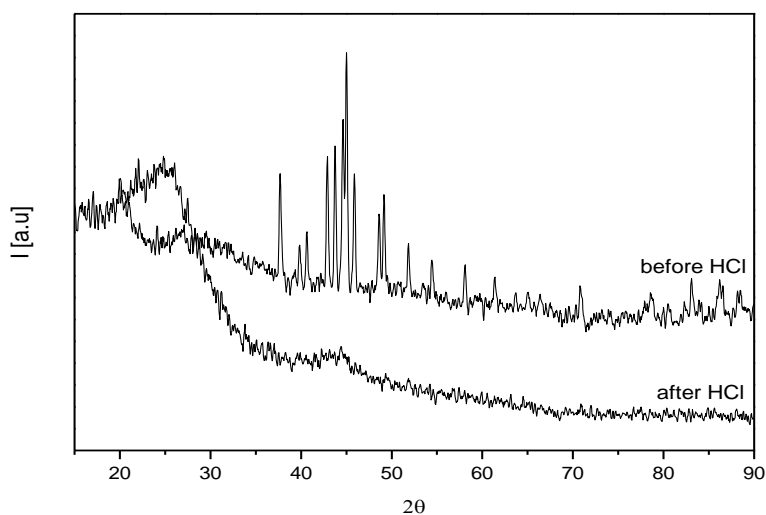


Figure 2. XRD patterns of FeDI1 samples prepared at 700°C, before (upper line) and after (lower line) treatment with 20% HCl.

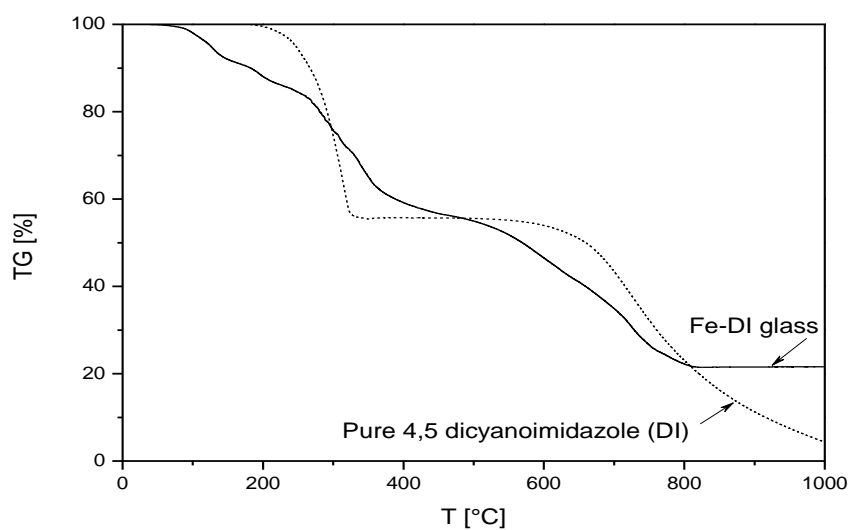


Fig. 3: TGA measurements of pure 4,5-dicyanoimidazole (dashed line) and iron-DI sample at R=1 (continuous line).

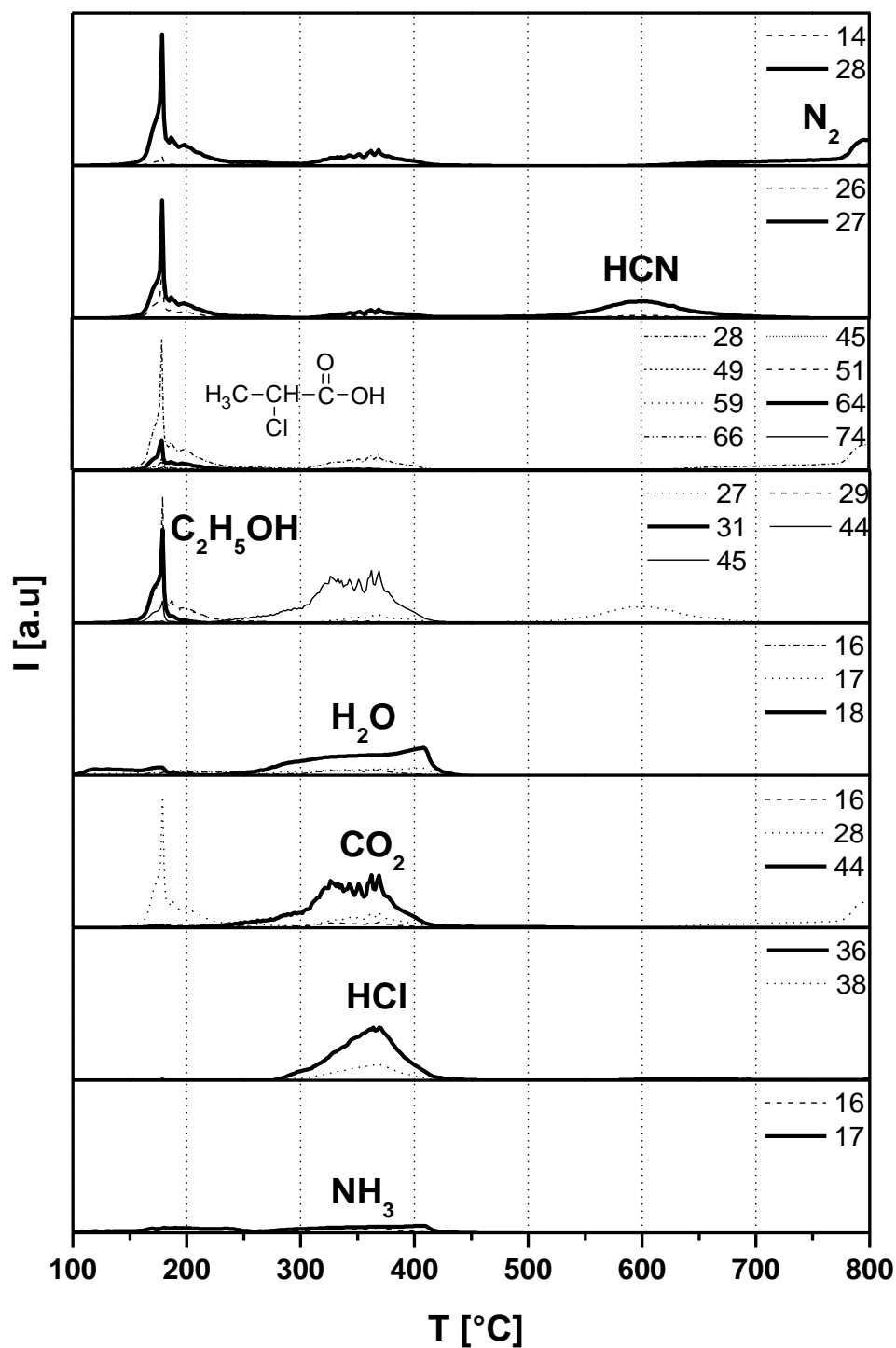


Fig. 4: Thermal decomposition of the Fe/DI starting material with following mass spectrometry. The measurement takes place under argon with a heating rate of 5 K/min.

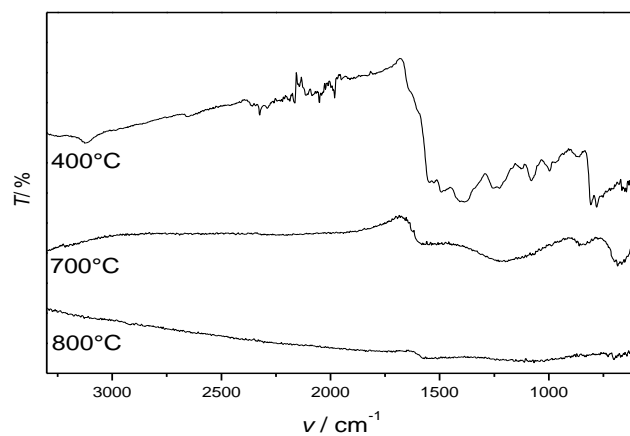


Fig. 5: IR spectra of Fe/DI samples R = 1 at different reaction temperatures.

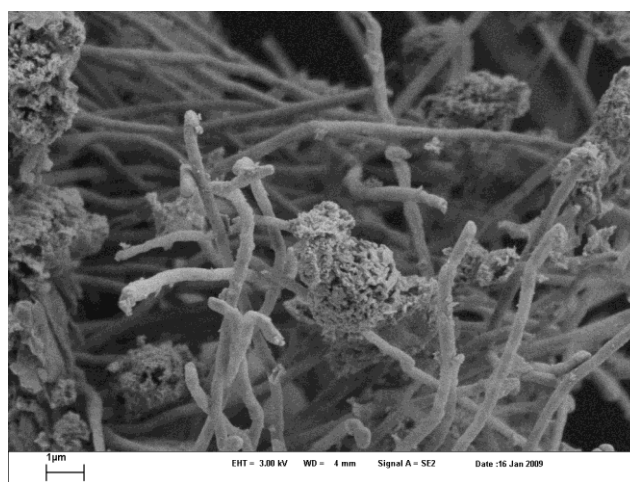
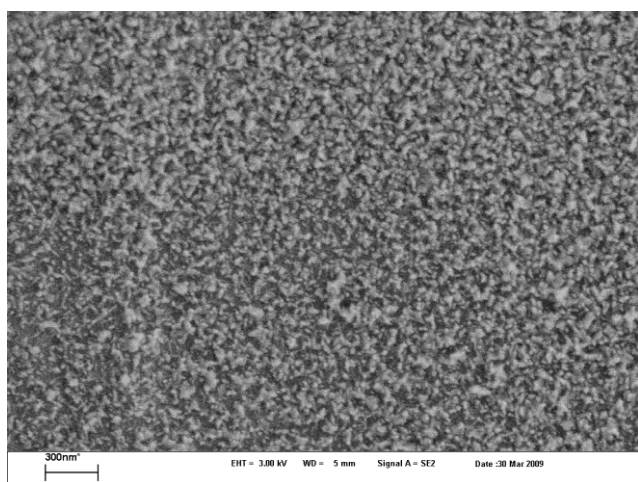


Fig.6: SEM images of samples prepared at different iron/DI molar ratios (R), in particular R=0.5 (left side) and R=2 (right side).

Experimental part

XRD measurements were performed on a D8 Diffractometer from Bruker instruments (Cu-K α radiation, $\lambda=0.154\text{nm}$) equipped with a scintillation counter. Elemental analysis was done for Carbon, Hydrogen, Nitrogen and Oxygen using a Vario EL Elementar and for iron, ICP-OES was done using a Vista-MPX CCD Simultaneous ICP-OES with radial plasma. TEM images were taken using a Zeiss EM 912 Ω operated at an acceleration voltage of 120 kV. Samples were ground and then suspended in ethanol. One drop of this suspension was put on a 400 mesh carbon-coated copper grid and left to air to dry. A HRTEM Philips CM 200 LaB $_6$, operated at an acceleration voltage of 200 kV was also used. SEM was performed on a LEO 1550 Gemini instrument. The samples were loaded on carbon coated stubs and coated by sputtering an Au/Pd alloy prior to imaging. TGA measurements were performed under nitrogen between 50 and 1000 °C (heating rate 10K/min) with a TG 209 F1 Iris®, Netzsch. Thermal decomposition with following mass spectrometry was done under argon with a ChemBET Pulsar TP/TPD automated chemisorption analyzer. Raman measurements were made using a WiTecConfocal Raman Microscope alpha300 R, frequency doubled green 532 nm Nd/YAG laser and Optical resolution diffraction limited to 200 nm laterally and 500 nm vertically, Spectral res. down to 0.02 wave numbers. Mössbauer spectra were obtained in backscattering geometry with the miniaturised Mössbauer spectrometer MIMOS II (REF) equipped with a ^{57}Co source, with a field of view of 15 mm diameter.